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Potassium Selective Quartz Crystal Microbalance Chemical Sensors using Functionalized Copolymer Coatings

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Abstract

Quartz crystal microbalance sensors that specifically detect K^+ ions have been developed using copolymers based on poly(acrylic acid) and functionalised with crown ethers to provide selectivity. The coatings selectively absorb K^+ over other Group I ions such as Li^+ and Na^+ . Sensors have been used in both batch and flow modes with detection limits in the region of 0.1-0.2 ppm for $K^+_{(aq)}$ with a linear range extending to over 1000 ppm. The sensors perform at least as well as other recently developed methodologies although further optimisation should significantly improve this performance.

Keywords: Quartz Crystal Microbalance; chemical sensor; acrylic acid copolymer; crown ether polymers; Group I ions.

Introduction

The development of new chemical sensors that are specific for particular chemical species is an active area of research [1,2]. Among the various transduction mechanisms available, there is considerable interest in piezoelectric sensors [3–5], often known as a *quartz crystal microbalance*, QCM where the resonant frequency of an oscillating quartz crystal is reported. This frequency change, ΔF , varies linearly [6] with an applied mass, M , according to the Sauerbrey equation.

$$\Delta F = (F_o^2 / A N \rho_q) M \quad (1)$$

where F_o is the fundamental oscillation frequency of the quartz crystal (in this work 10 MHz), A is the active area of the gold, N is a constant for the particular grade of quartz and ρ_q is the density of quartz.

While it is well known that Equation (1) is at best an approximation, it is adequate so long as the frequency change is limited to $< 0.02 F_o$ and the fluid in which the crystal operates causes low acoustic loss. Greater absolute accuracy can be achieved by measuring the impedance changes across the crystal rather than the simple frequency change [7, 8] but for straightforward work, particularly where the system may readily be calibrated, the Sauerbrey equation is satisfactory.

The major drawback of the QCM is a lack of selectivity to the source of the mass changes. The surface of a resonator can be modified with a film to selectively bind a particular species and a number of approaches have been reported. These include coating the crystal with responsive materials or molecularly imprinted polymers [9]. QCM's have been become well established in sensing regimes such as gas and vapour phase work [10 -13] and in solution despite the lower resolution caused by the viscous damping of the oscillation by the liquid. Examples include immunoassays [14], electrochemical analysis [15], ion binding [16], and determination of trace dissolved organics [17, 18].

The approach that has been adopted in our laboratory involves coating the crystal with a functionalised polymer to target metal ions in aqueous solution. Operation in solution places constraints on the system to be used. Particular requirements of such systems include a high loading of chelating ligand to ensure good sensitivity as well as rapid mass transfer. This can be achieved by using a coating that is highly compatible with the solvent so that it swells and allows solvent and analyte to permeate through. Coating with a functional monolayer would be relatively straightforward but the use of a functionalised polymer means that a larger loading can be obtained per unit area of the crystal. To prevent the coating from dissolving, it can be crosslinked although anchorage to the crystal via covalent bonds would give better long-term stability. It is well known that sulphur containing moieties can self-assemble and be irreversibly attached to clean gold surfaces [19]. The approach is illustrated schematically in Figure 1. In principle, this should give improved sensitivity and speed of response over systems where the chelator is simply dissolved in a water insoluble matrix such as PVC.

The success of the general approach was demonstrated by the development of polymer based QCM sensors for Cu^{2+} [20] and for Ni^{2+} [21, 22] with detection limits in the region of 0.1 ppm and reasonable, although not optimised, selectivity. Another potential target [23] is the analysis of Group I metal ions such as sodium or potassium so that it was decided to investigate sensors based on crown-ether containing copolymers.

The polymer coating on the crystal is based on a cross-linked version of a water compatible poly(acrylic acid) containing crown-ether substituents [24]. The metal-ion binding properties of a number of crown-ether copolymers have been investigated by Kimura *et al.* [25] who showed that the copolymers reflect, and in some cases enhance, the binding properties of the free crown-ether rings. For this reason the polymers used as the basis for the work reported here. The crown-ether moieties selectively chelate metal ions with an ionic radius compatible with the diameter of the crown-ether ring [26] so changing the size of the crown ether ring

modifies the selectivity of the polymer coating. This selective chelating potential has been well documented since the pioneering work carried out by Pedersen [27] in the mid 1960's.

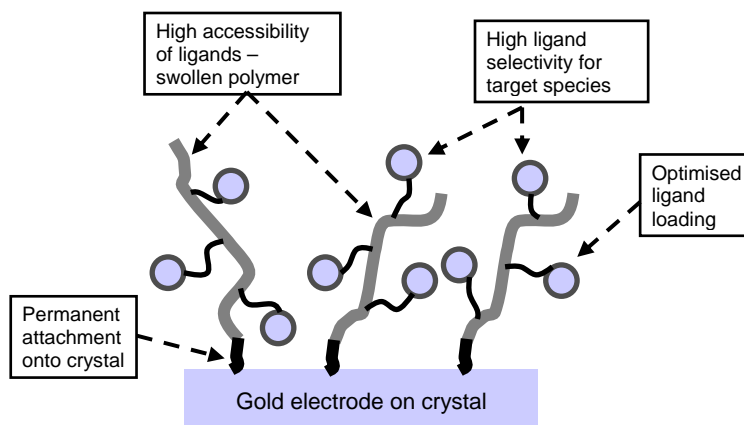


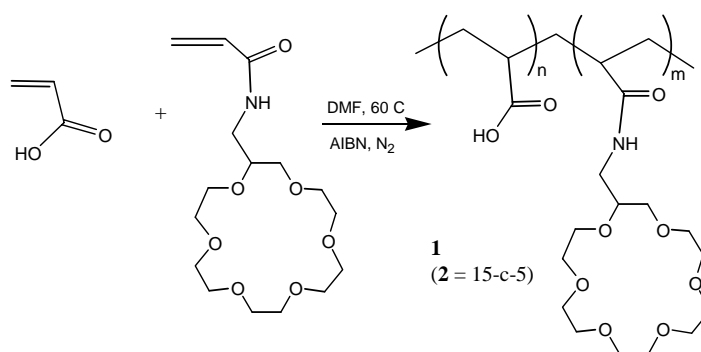
Figure 1. The design criteria for a selective polymer based piezoelectric

This paper describes the characterisation of QCM sensors coated with crown ether containing acrylic acid copolymers in terms of their ion-binding properties and their potential for quantitatively sensing K^+ ions in aqueous solution.

Experimental

Synthesis of polymer coatings

The polymer used as the basis of the selective coating is a copolymer of acrylic acid and a crown ether functionalised acrylamide shown in Scheme 1. This was selected to give a water compatible system which would swell in contact with water to give ready access for analytes to absorption sites. Materials containing two crown ethers, 15-c-5 and 18-c-6 were used. The synthesis of the monomer and detailed chemical characterisation of the polymers has been described previously [28].



Scheme 1. Synthesis of crown ether containing polymers

Since the amount of polymer on a crystal is very low, in order to measure the ion uptake and selectivity of the polymer systems, powdered, cross-linked resins were prepared using ethylene glycol dimethacrylate containing the same loading of crown ether. A “blank” copolymer was also synthesised by [28] omitting the crown ether. The composition of the resins and the crown-ether loadings are shown in Table 1.

Table 1. Composition* of the acrylic acid based chelating resins.

Resin	Crown ether	% Crown-Ether [#]	% EGDMA	% Yield
15c5-70	18-c-6	8	70 %	84 %
15c5-30	18-c-6	11	30 %	99 %
15c5-2	18-c-6	13	2 %	82 %
18c6-70	15-c-5	10	70 %	74 %
18c6-30	15-c-5	13	30 %	69 %
18c6-2	15-c-5	11	2 %	83 %
PAA	-	0	70 %	94 %

* all percentages are based on w/w values.

[#] the loading of crown ether in the recovered polymer was $\pm 2\%$

Preparation of sensor crystals

The piezoelectric crystals were 15 mm diameter AT-Cut, quartz crystals (ICM Co, Inc, Oklahoma City, Oklahoma, USA) with a fundamental frequency of 10 MHz and 4.5 mm diameter circular electrodes (50 Å Cr under-layer covered with 1 µm gold layer) on either side. The electronic driving circuits were built in-house and have been described previously [21]. They operate by comparing the frequency of a crystal with that of a reference crystal, the frequency difference being monitored.

Crystals were cleaned prior to use with piranha solution (1:1 ratio of 98% sulphuric acid and 40% H₂O₂), and rinsed with Milli-Q 18.2 MΩcm, water. After drying, the resonance frequency was recorded in air and this used as the 'clean' frequency. An potential complication is the conducting solution. To eliminate potential effects due to changes in the conductivity of the solutions, the crystal mountings were coated in non-conducting polymer. The reference crystal was also placed in an identical mount and included in the solution to cancel any other effects.

The crystals were coated by dipping into 30 cm³ of a 5 mM solution of 2-amino-ethanethiol in ethanol until the resonant frequency became stable. This formed a self-assembled monolayer on the gold, onto which the polymer could be reacted to form a bound coating. 0.5 cm³ of a monomer or polymer solution was dropped onto QCM crystal and heated to 75 °C for several hours to polymerize. After cooling the coated crystals were rinsed with hot acetonitrile followed by hot methanol and the resonance frequency recorded. They were then set in a mount where one face was sealed into a glass chamber so that only one side of the crystal came into contact with the solution.

Metal ion absorption experiments

Stock solutions of 50 ppm of Na⁺_(aq), Li⁺_(aq) and K⁺_(aq) sulfates or chlorides were prepared from

Analytical grade dried materials. Aliquots of 50 cm³ of the stock solutions were placed into volumetric flasks and 1g of the precipitated, cross-linked resin added. After equilibration for several hours, the concentration of the metal ions were measured using Atomic Emission Spectroscopy, AES, on a Varian AA275 instrument.

Characterisation of sensor behaviour

For batch mode measurements, the coated crystal was placed in a mount [21] in 30 cm³ of pure water and allowed to stabilise. Metal ions were then added to the water via the injection of a metal sulphate stock solution (10 – 100 ppm) and the change in resonant frequency followed. The system is also suitable for operation in a flow mode where coated crystals were incorporated into a flow injection analysis set-up, (FIA) with a flow rate of 1.0 – 2.0 cm³ s⁻¹ and tube diameter of 5 mm. The crystal was allowed to stabilise in a steady flow of Milli-Q_{plus} 185, 18.2 MΩcm water and injections of 5 – 40 μL of the stock solutions made as the frequency was monitored.

Results and Discussion

Chelating ability of the copolymers

Samples of crosslinked, powdered polymers were pre-swollen in water after which the equilibrium absorption of Li⁺, Na⁺ and K⁺ from 50 ppm aqueous solutions was measured and is shown in Figure 2. The change in solution concentration with time was monitored by AES. Monitoring the rate of ion uptake showed that the absorption was complete within 2 minutes.

The absorption of K⁺_(aq) was larger than that for Na⁺_(aq) or Li⁺_(aq) for each of the materials used. Those containing 18-c-6, showed the largest uptakes of approximately 1 mg K⁺ per gram of copolymer. This is expected from the better match in cavity size. [26],[28] so the K⁺ ions bind more effectively and are retained in the copolymer network. The degree of crosslinker

included in the copolymerization had little effect on the absorption of ions. The polymers containing 15-c-5 showed some uptake of $K^+_{(aq)}$ but much larger $Na^+_{(aq)}$ uptake than the equivalent 18-c-6 network. Again, this behaviour mirrors that of free crown ethers in solution [28]. The unfunctionalised resin containing no crown ether had little uptake capacity, presumably due to some ion-exchange effect with acid groups, but no selectivity for the ions involved here.

The calculated K^+ / Na^+ selectivity is 13.1, 13.1 and 13.8 for the three 18-c-6 containing copolymers in comparison with 3.6 – 4.3 for the 15-c-5 resins and 2.1 for the resin containing no crown ether. The first of these is therefore much more selective.

In order to confirm that this selectivity would be retained in solutions containing mixtures of ions, competitive uptake studies were conducted. Figure 3 shows the results for absorption from a solution containing all three ions. The polymer with no crown ether again absorbed no significant amount of any of the ion. The 15-c-5 polymers absorb similar amounts of $Na^+_{(aq)}$ and $K^+_{(aq)}$ from the single solutions (Figure 2) but only K^+ is taken up in competitive absorption. Also, for 18-c-6, when both $Na^+_{(aq)}$ and $K^+_{(aq)}$ are available for chelating only $K^+_{(aq)}$ is taken up. This further confirms the selectivity of both copolymers for $K^+_{(aq)}$ over $Na^+_{(aq)}$.

These results demonstrate the potential of the resins to act as ion-selective membranes. The 18-crown-6 copolymers showed a high degree of selectivity for $K^+_{(aq)}$ and a response time of less than 60 seconds. Thus, this system was selected for further study as a potential sensor.

Application of the copolymers as a sensor

Two series of crystals were investigated; one coated with a copolymer functionalised with 10% 18-c-6 and a 'blank' copolymer containing no crown-ether. They were coated from solutions with concentrations controlled so as to give film thickness between 70 - 200 nm, this requiring ~ 1 mg of polymer. Thicker films caused overloading of the crystals and failure of the system.

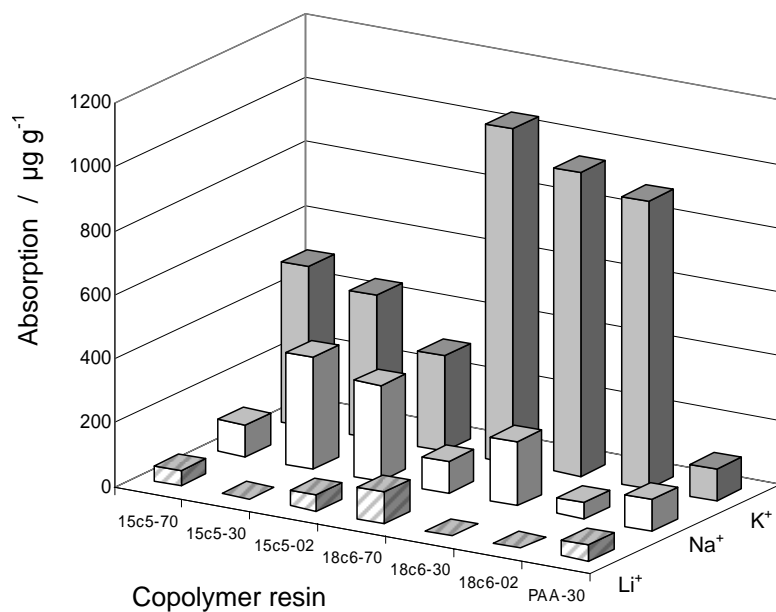


Figure 2. The uptake of aqueous metal ions from 50 ppm solutions of metal ions

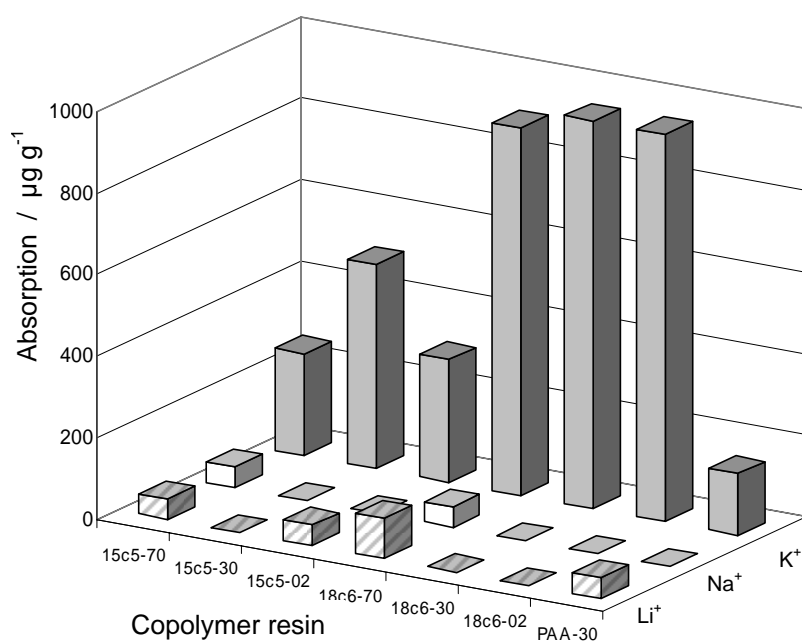


Figure 3. The competitive uptake from a solution containing 50 ppm of each ion

Figure 4 shows the response of a copolymer coated crystal to the addition of K^+ ions to the solution. After the frequency stabilised while immersed in 30 cm³ water, successive 10 μ L injections of a stock solution were made, each injection changing the concentration by 3 ppm. The resonance frequency increased instantaneously by about 10 Hz for each successive injection. To ensure rapid mixing, a magnetic stirrer was used but the stirrer speed had no effect on the value or stability of the resonance frequency.

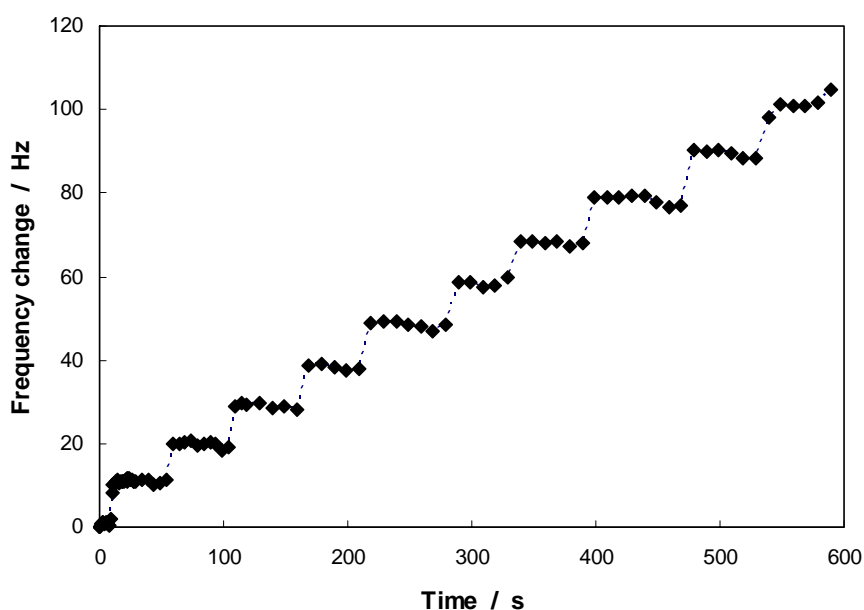


Figure 4. The response of 18-c-6 functionalised QCM to successive additions of 10 μ g K^+

The response of the QCM to addition of the three metal ions is shown in Figure 5. The response to $Li^+_{(aq)}$ or $Na^+_{(aq)}$ was negligible but $K^+_{(aq)}$ produced a significant, reproducible response. From the slope of the plot, a response factor of 0.7 Hz ppm⁻¹ can be calculated. The optimised frequency stability is ± 0.30 Hz, giving an estimated sensitivity of ~ 0.4 ppm. As a control, the experiment was repeated using a polymer coating containing no crown ether. As shown in Figure 6. There is no difference in response for the three ions. The selective binding

properties of the crosslinked copolymers discussed above were successfully transposed to the thin coating of the QCM crystal.

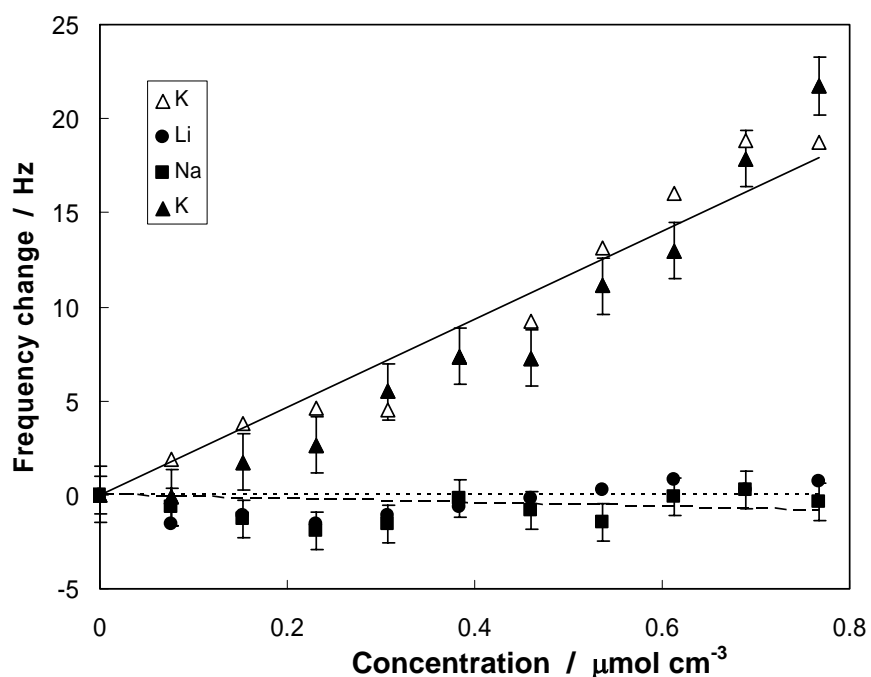


Figure 5. Concentration dependence of 18-c-6 functionalised QCM response on addition of metal ions.

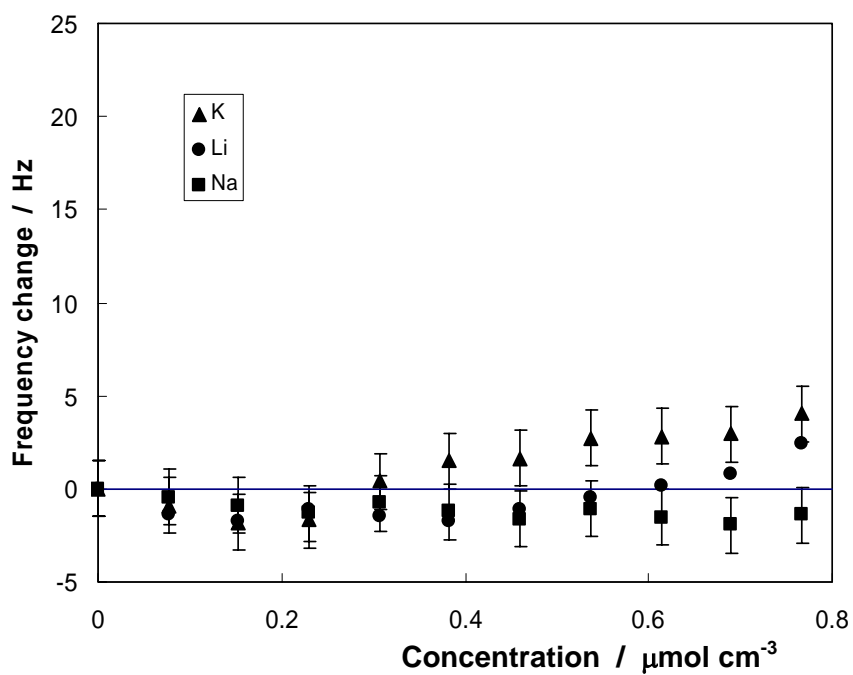


Figure 6. Concentration dependence of unfunctionalised QCM frequency change on addition of metal ions.

To investigate the range over which the sensor could be used, the results shown in Figure 7 were recorded. The $K^+_{(aq)}$ response rises linearly up to a concentration of ~ 35 mM, corresponding to a solution of ~ 1350 ppm and plateaus thereafter, presumably due to saturation of the available adsorption sites. Further analysis of the absorption capacity in terms of the Langmuir model has been detailed previously. [28]

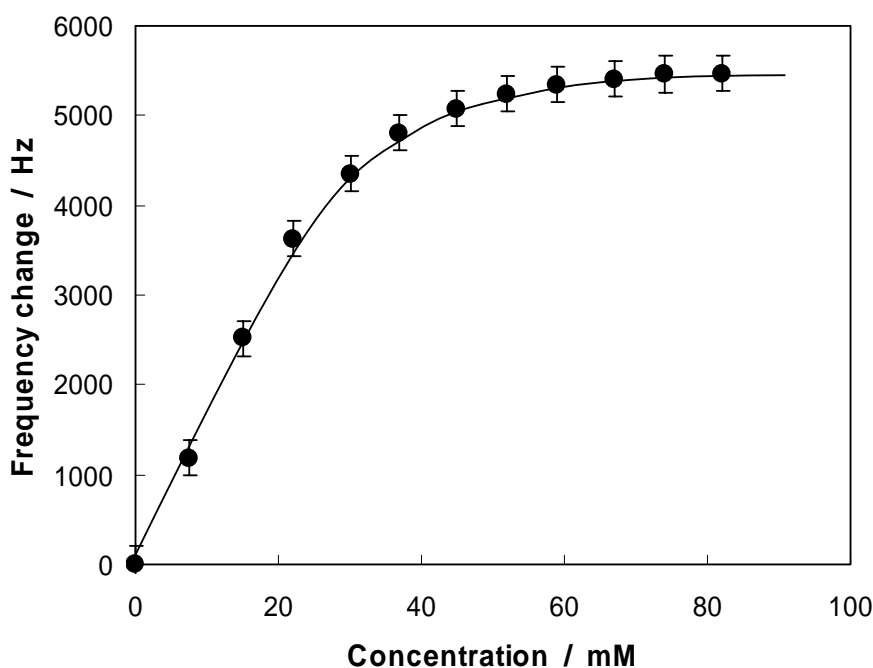


Figure 7. Concentration dependence of 18-c-6 functionalised QCM frequency change on addition of K^+ ions.

In addition to use in batch mode, the sensing characteristics have been determined in a flow system. After stabilisation of the frequency in the flow system, known volumes of the metal ion solutions were injected. The onset of frequency changes corresponded to the expected time for the sample to flow from the injection port to reach the crystal surface. Figure 8 shows examples of the elution profiles obtained for injections of K^+ resulting from absorption by the polymer coating. The responses were characterised by a rapid rise but slower desorption. A linear correlation ($r^2 = 0.98 - 0.99$) was observed between the peak height and the volume of K^+ injected. Results for the unfuctionalised “blank” crystal are shown in Figure 9. The normalised

response profiles of the crystal to $\text{Li}^+_{(\text{aq})}$, $\text{Na}^+_{(\text{aq})}$ and $\text{K}^+_{(\text{aq})}$ were obtained and the crystal showed no uptake for any of the ions investigated. The same procedure was used to assess the response of the crown-ether coated resonator, the results being shown in Figure 10. The coating introduced a small response to $\text{Na}^+_{(\text{aq})}$ while remaining unresponsive to Li^+ . However, there was a large response to K^+ mirroring the selectivity shown when operated in batch mode. From the slope of the plot, a response factor of 1330 Hz cm^{-3} can be calculated. Taking into account the dilution in the FIA system, this gives an estimated sensitivity of 0.4 ppm.

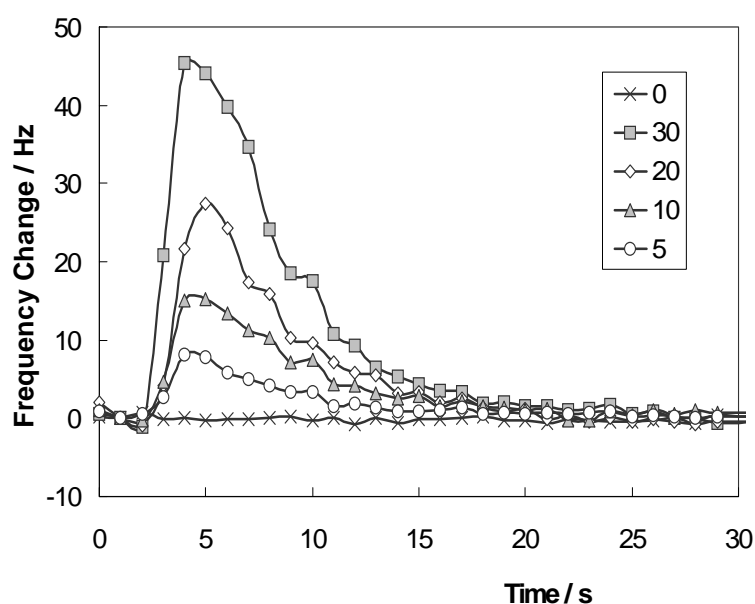


Figure 8. Response profiles for QCM coated with 18-c-6 containing copolymer to the injection of aliquots of $\text{K}^+_{(\text{aq})}$. The legend shows the injected volume in μg .

The frequency change of the non-functionalised crystals is believed to be associated with changes in the capacitive and viscoelastic properties of the oscillating medium. The resonant frequency of an oscillator operating in a liquid environment is related to the density, viscosity and ionic concentration of the solution. For the purpose of the work carried out in this paper the precise origin of the frequency response is of limited interest. The important observation is that a reproducible response exists and that this response is associated with the presence of the functionalised polymer and K^+ ions. The relationship between frequency change and absorbed

mass will not be straightforward over a large concentration range and will not be given to any degree of accuracy by Equation (1). However, the system is easily calibrated by measuring the response to solutions of known concentration, akin to the use of a pH meter or other ion-selective electrode.

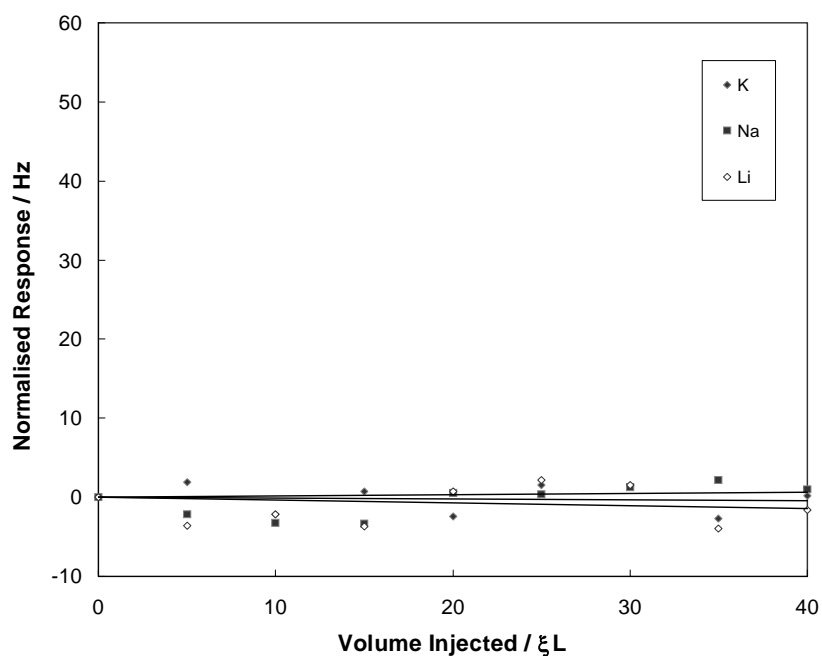


Figure 9. Normalised response of unfunctionalised polymer crystal to Group I metal ions.

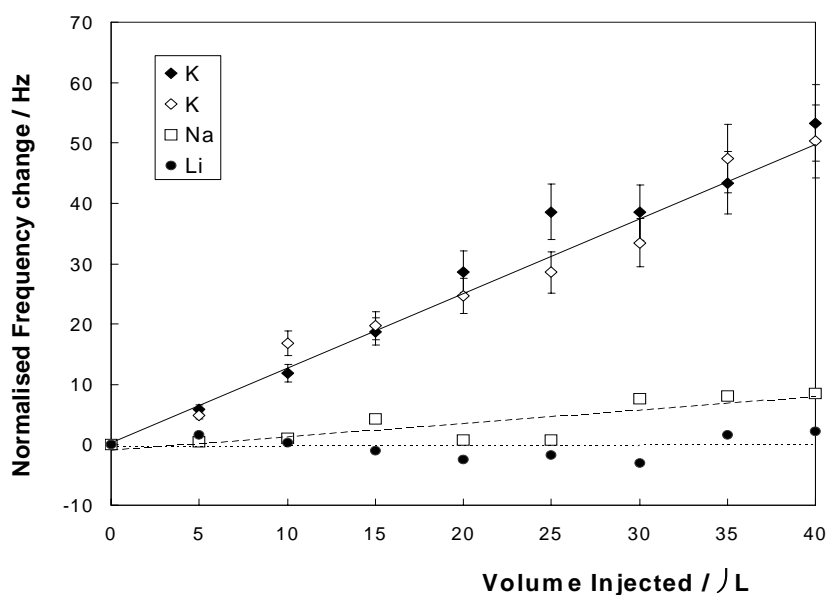


Figure 10. Normalised response of 18-c-6 copolymer crystal to Group I metal ions.

The selectivity and sensitivity of this method are comparable with methods such as ion-selective electrodes. Optimisation of the coating in terms of the level of crown ether gives an avenue to increase the sensitivity. At present, the frequency response is stable to only ± 0.5 Hz. With better design of the FIA and improved mountings for the crystal, the sensitivity can reasonably be expected to increase. The current response rate is also too slow for routine operation and optimisation of factors such as film thickness should allow improvements.

The sensor developed had an estimated detection limit of 0.2 ppm and a linear response range of 0-1000 ppm with zero response to either $\text{Na}^+_{(\text{aq})}$ or $\text{Li}^+_{(\text{aq})}$. These values are well within the operating criteria for commercial K^+ sensors. The markets for such devices are in the areas of water analysis and physiological sensors. The concentration of K^+ in tap-water is typically in the range of 1-80 ppm. In the human body the concentration of K^+ in blood serum is around 140 ppm and bile around 500 ppm with the most common interference arising from Na^+ . The performance of the sensors illustrated here are at least comparable with other recently published attempts to develop potassium selective sensing systems [29, 30] but potentially offer more flexibility in use.

Conclusions

A new class of polymer coatings with high specificity for K^+ ions over other Group I metal ions has been developed and used as the sensing layer in QCM's. The polymers utilise 18-crown-6 rings copolymerised with acrylic acid to selectively bind K^+ ions. In cross-linked resins, the materials show good selectivity and they were readily coated onto QCM crystals where the same selectivity was observed. In batch mode, the sensor had an estimated detection limit of 0.2 ppm and a linear response range of 0-1000 ppm with zero response to either $\text{Na}^+_{(\text{aq})}$ or $\text{Li}^+_{(\text{aq})}$. When used in a flow system, the sensitivity was estimated to be ~ 0.4 ppm although after optimisation this should be considerably improved upon.

The results further illustrate the validity of our approach in using functionalised polymer coatings covalently attached to QCM crystals using self assembled monolayers. It extends previous examples involving transition metal ions. Such sensors possess the required selectivity and stability to operate in the ppm range. With improved design this should be extended to one part in 10^9 . The copolymer system incorporated in the sensor design can be readily modified to include a variety of different host compounds and offers a general route to the production of an array of selective chemical sensors.

Further work is necessary to completely characterise the sensor behaviour in terms of the lifetime and long-term stability of such sensors. However, the approach gives a potentially highly flexible method for producing QCM sensors.

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